Plane-wave DFT Investigations of the Adsorption and Activation of CO on Fe_5C_2 Surfaces

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Supporting Information Material

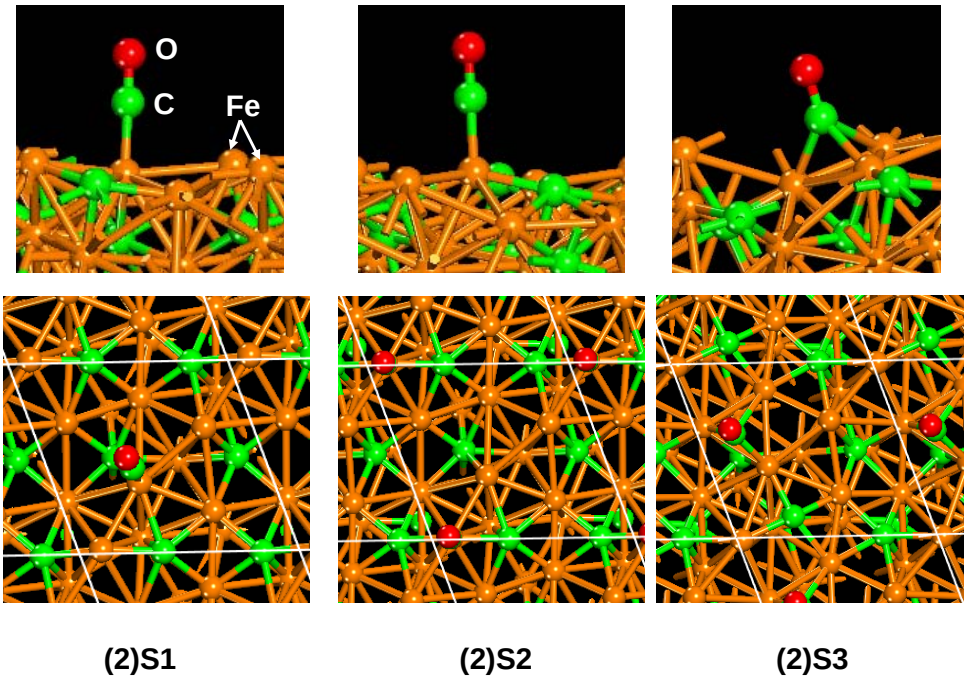

Figure S1. Side and top views of additional adsorption configurations of CO on (010)0.25 surface of χ-Fe_5C_2. The left ((2)S1) and central ((2)S2) panels indicate two different on-top binding configurations while the right panel represents a three-fold state ((2)S3).

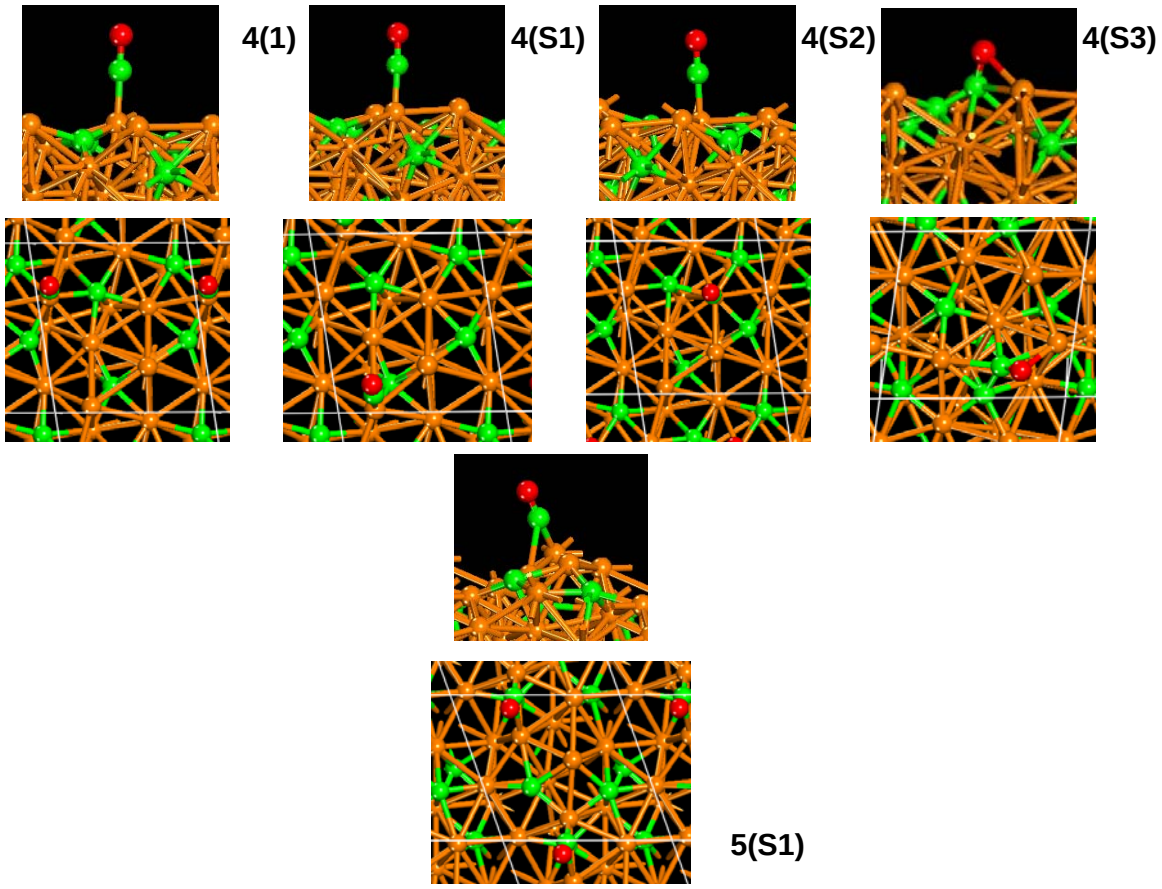

Figure S2. Side and top views of additional adsorption configurations of CO on (111) 0.00 (panels (4)1-4(S3)) and on $(11\bar{1})0.50$ (panel 5(S1)) surfaces of χ-Fe_5C_2. Configurations 4(1), 4(S1), 4(S2) represent binding states of CO on-top of Fe atoms while configuration 4S(3) indicates a 5F-C adsorption structure having a total of five bonds with the Fe atoms and one bond to a surface C(s) atom. Configuration 4(1), which is also represented in the main paper in Figure 3, is also included here in order to clarify its location relative to the other on-top adsorption sites.

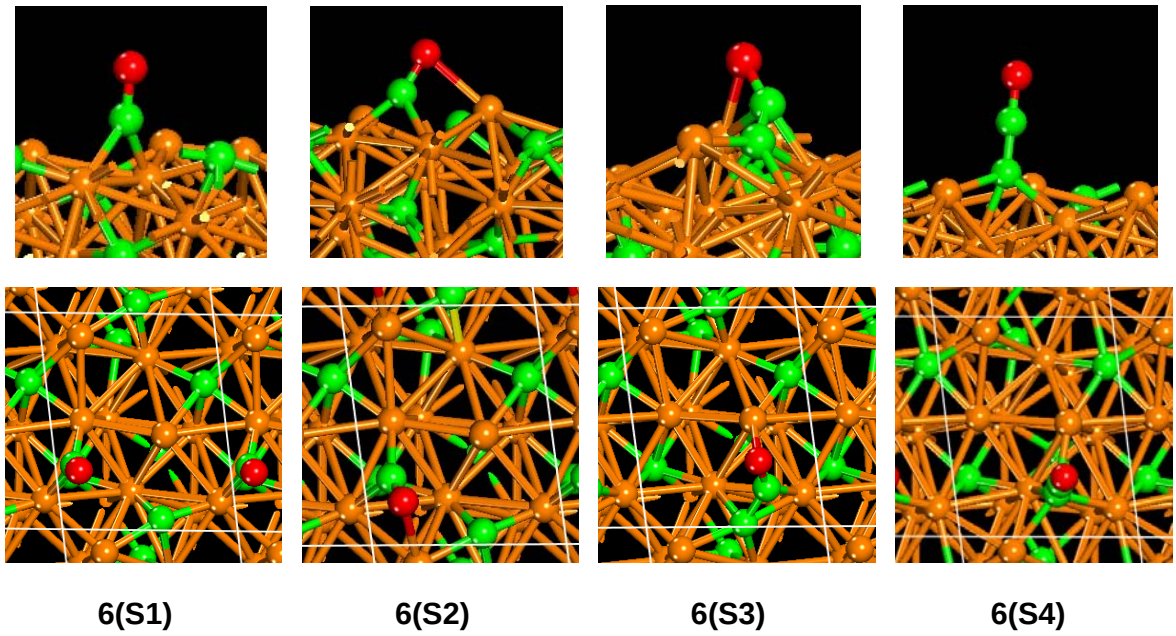

Figure S3. Side and top views of the additional adsorption configurations of CO on (110) 0.50 surfaces of χ-Fe_5C_2. These atomic configurations correspond to adsorption in a 2F state (6(S1)), 3F state (6(S2)), 3F-C state (6(S3)) and 0F-C state (6(S4)), respectively.

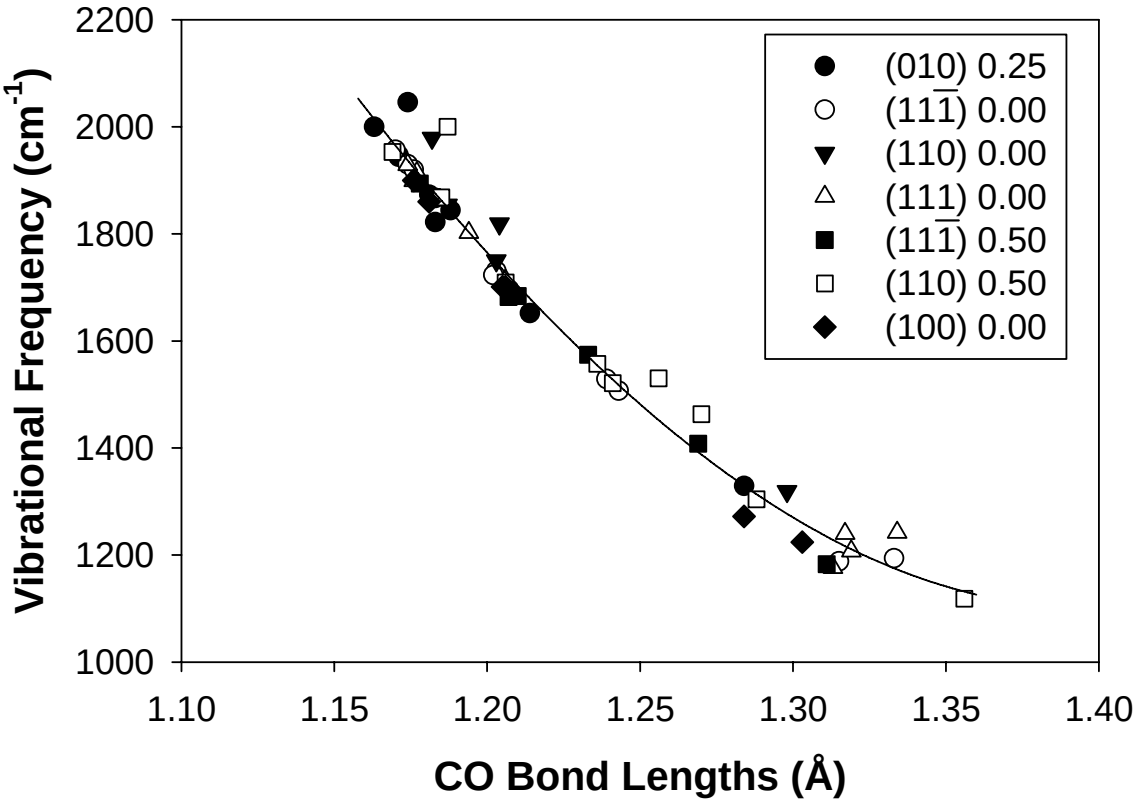

Figure S4. Variation of the CO vibrational frequencies as function of the corresponding bond lengths for different adsorption configurations identified in the current study. The indicated line represents an inverse second order polynomial fit of the data.

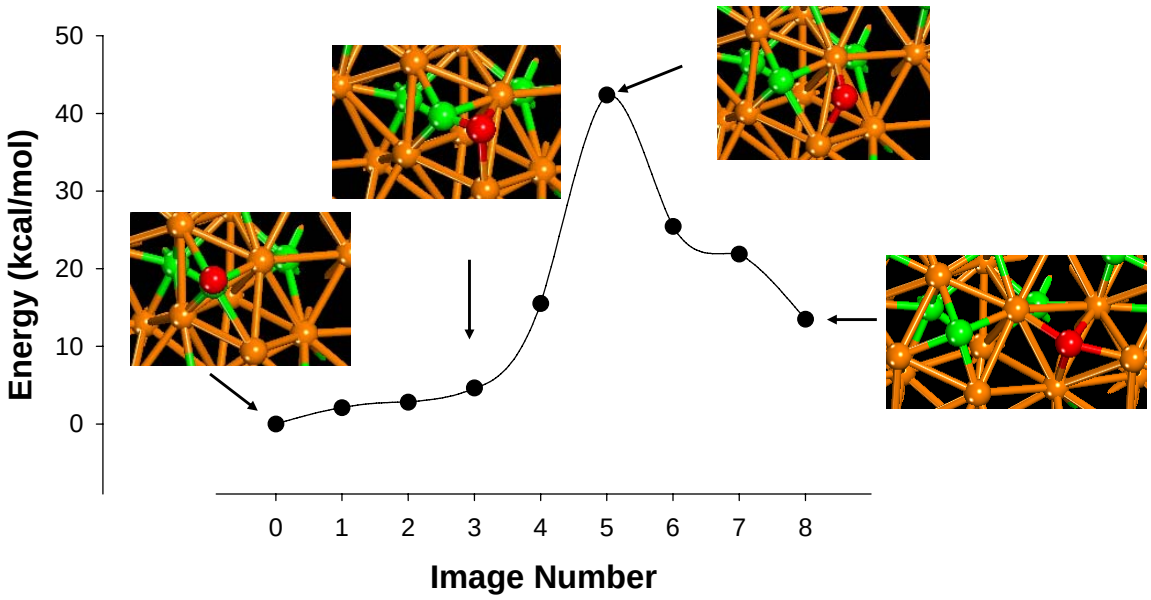

Figure S5. Minimum energy pathways for CO dissociation on $(11\bar{1})0.50$ surface starting from a (5)3 4F type adsorption configuration. In the final state both the C and O atoms are adsorbed at pseudo four-fold sites.

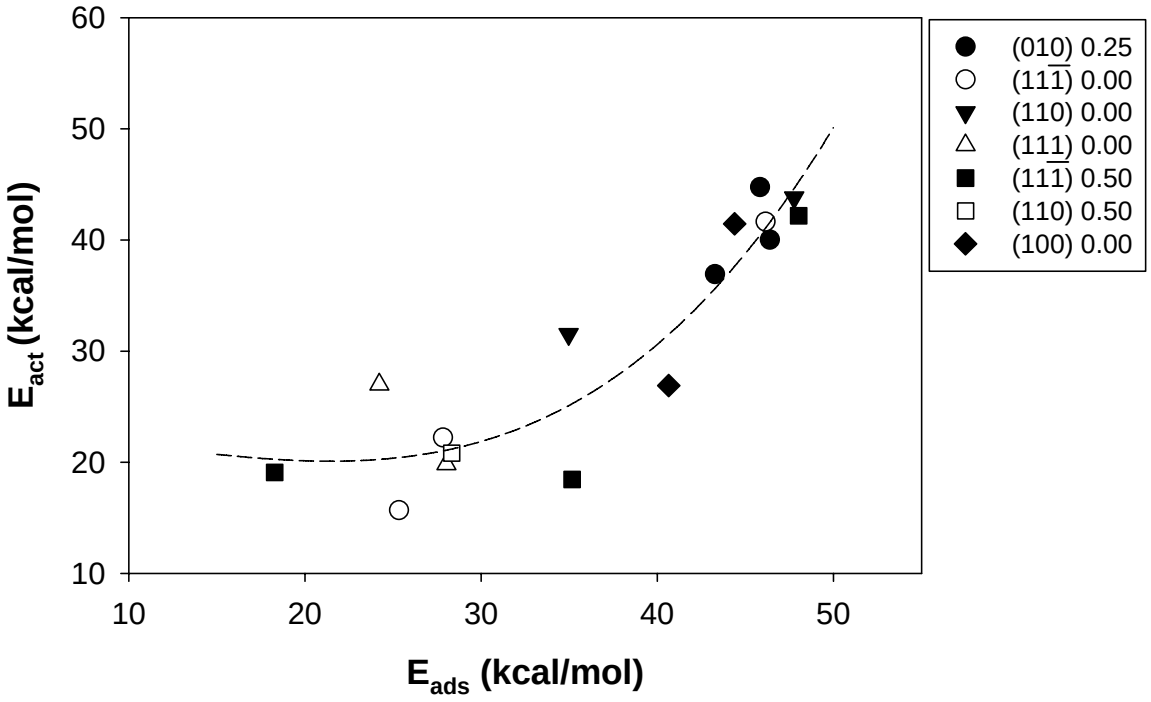

Figure S6. Variation of the CO activation energy as function of the corresponding adsorption energy in the initial state for various Fe_5C_2 surfaces considered in this study. The dotted line represents a second order polynomial fit of the data, intended to provide a general guide for the eye.